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CHARACTERISTICS OF RARE METALS FROM THE STANDPOINT OF OCCUPATIONAL HYGIENE

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Occupational, or labor hygiene is confronted with the problem of studying labor conditions in the mining and utilization of rare metals. In connection with the problem's comparative novelty, the Chair of Labor Hygiene of the First Moscow Medical Institute has approached it by studying systematically the general hygienic characteristics of rare metals. With this in mind, the following information was compiled and is presented below in the following order: name of the metal, its principal mineral sources, and its applications in industry.

Lithium: lepidolite, spodumene, petalite, triphylite; production of hard alloys (Scleron, antifriction alloys), producing opal glass in pyrotechnology, enamels, varnishes, medicine, electrical engineering, etc.

Gallium: zinc blende, bauxite, kaolin; high-temperature thermometers for electrical engineering, medicine.

Indium: zinc blende, pyrite, wolfram and tin ores; coating nonferrous metals, coating searchlight reflectors, lighting reflectors, addition to various alloys.

Thallium: lorandite, small quantity contained in ores of zinc, lead, iron, and mica, carnallite; acid-resisting alloys, liquid amalgam for thermometers, glass industry, photoelements, medicine.

Titanium: rutile, ilmenite, titanomagnetite, small quantities in almost all rocks; smelting high-grade steels in metallurgy, catalyst in production of dyes in the chemical industry, refractories, textile industry.

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Zirconium: baddeleyite, zircon; producing alloys in metallurgy, enamels, refractories, medicine.

Vanadium: vanadates and sulfovanadates (patronite, vanadinite), titanomagnetites; special steels in metallurgy, alloys with Al, Ni, Wo, catalyst and oxidizer in chemical industry, glass industry, aniline dye and photographic industries.

Niobium: niobite, samarskite, "Loparite," "Ferasmanite"; cathodes of powerful oscillators for radio engineering, in hard cutting alloys.

Tantalum: tantalite, "Loparite," "Ferasmanite"; hard and acid-resisting alloys, special steel, radio engineering, cutting tools, platinum substitute.

Molybdenum: molybdenum glance (MoS_2), "Wolfenite" ($PbMoO_4$), lead ores; special steels in metallurgy, hard alloys, acid-resisting alloys, X-ray tubes, catalyst in chemical industry.

Wolfram: wolframite, scheelite; special steels in metallurgy, very hard alloys, acid-resisting alloys, incandescent bulbs for electrical engineering, arc lights, X-ray tubes.

Cobalt: asbolite, cobaltite, etc.; hard alloys in metallurgy, special steels, dye industry, chemical catalyst.

Antimony: antimony glance Sb_2S_3; type metals and other alloys, textile industry, medicine, enamels.

Cadmium: zinc blende and other zinc ores; various alloys, textile industry, medicine.

The toxicological properties of the more important rare metals are listed briefly below.

1. Thallium is found in the following forms: $TlCl_2$, thallium chloride; Tl_2SO_4, thallium sulfate; and $TlCl_3$, thallic trichloride. Thallium is used in medicine as an epilatory in the treatment of dermatomycoses.

Continuous exposure to thallium salts changed partial alopecia into complete baldness in animals. High concentrations of thallium cause intoxication in rabbits characterized by anorexia, emaciation, diarrhea, stomatitis, and, in severe cases, convulsions and tremors. Death occurs after 10 to 15 days. Cataracts are observed in rats; in young animals, growth is inhibited and rickets is observed. Thallium is deposited in the muscles. Toxic phenomena, and occasionally death, have been noted in the therapeutic use of thallium.

Symptoms of toxic effect: neuritic arthralgia and myalgia, dystrophia, acromelic neuritis (podal), cephalalgia, insomnia, depression, irritability, injury to the optic nerve, anorexia, nausea, vomiting, stomatitis, hypersalivation, albuminuria, and uremia.

Early symptoms are changes in the hemogram (lymphocytosis and eosinophilia).

2. Indium is found in the following forms: $InCl_3$, indium trichloride; $In_2(SO_4)_3$, indium sulfate; $In(NO_3)_3$, indium nitrate; $In_2(CO_3)_3$, indium carbonate; $InCO(CH_3COO)_3$, indium acetate; and $In(OH)_3$, hydrate of indium oxide. In pharmacology it is considered an epilatory.

Indium has an astringent effect upon the mucous membranes. It is used in the form of salts to treat mycoses and to change the color of animal skins. There have been experimental attempts to use indium salts for the treatment of syphilis, tuberculosis, trypanosomiasis and relapsing typhus, but results were unsatisfactory.

Metallic indium when introduced intramuscularly and intraperitoneally does not have a toxic effect. Indium salts introduced per os are very slightly toxic. Continuous introduction of large doses (117-176 milligrams) of indium sulfate in rats causes emaciation and sluggishness. Hypodermic injections of indium salts in mice (60 milligrams) and rabbits (150 milligrams per kilogram) causes intoxication characterized by diarrhea, hemorrhages (nose and intestinal), albuminuria, and acromelic paresis. Necrosis sometimes appears at the site of injection. Intoxication frequently ends in death.

3. Vanadium is found in the following forms: V_2O_3, vanadic oxide; VCl_3, vanadic trichloride; VO_2, vanadium dioxide; VCl_4, vanadium tetrachloride; V_2O_5, vanadium pentoxide; and various salts of vanadic acids. It is used in medicine to treat syphilis. Vanadium and its compounds, when introduced per os in animals, cause diarrhea and acromelic paralysis (posterior). Ammonium vanadate, in a dose of 4-9 milligrams per kilogram, causes severe pain in animals and results in death. When cats inhale vanadium pentoxide, irritation in respiratory passages, anorexia, and bloody stools are observed.

The action of vanadium pentoxide is very sharply expressed, causing injury to the nervous system (cephalalgia, vertigo, hysteria, blindness due to injury to the optic nerve). Poisoning by vanadium pentoxide may be lethal. Vanadium salts cause similar phenomena, differing only in intensity. Hemorrhagic nephritis is possible. Metallic vanadium vapors cause vertigo and irritation of the respiratory passages.

4. Molybdenum is found in the following forms: MoO_2, brown molybdenum dioxide; MoO_3, molybdic anhydride; MoS_2, molybdenum sulfide; Na_2MoO_4, sodium molybdate; $(NH_4)_2MoO_4$, ammonium molybdate; and $CaMoO_4$, calcium molybdate. According to the data of several authors, molybdenum is a valuable biologic element. It is contained in small quantities in animal and plant tissues. The largest amount is in the liver. It stimulates the growth of young animals. It is necessary to certain bacteria and algae in order to fix molecular nitrogen from the air. Plants absorb it from the soil.

In pharmacology, sodium molybdate is considered a bactericide. It is used (without particular success) to treat tuberculosis of the skin and septic wounds.

Metallic molybdenum and molybdenite (MoS_2) are not toxic. Molybdic anhydride and salts of molybdic acid are toxic. When introduced per os or otherwise, the action on the gastrointestinal tract is very sharply expressed; vomiting and bloody diarrhea develop. Convulsions and tremors are observed when the nervous system is affected. Lethal doses are quite high: 0.25 gram for dogs and 2.20 grams for guinea pigs per kilogram of weight. Chronic action is the same as in acute, but the symptoms are not so strong.

Colitis and albuminuria are observed in the treatment of tuberculosis by a molybdenum preparation (molyform).

The palmar skin of those handling molybdenum wires in factories is colored blue.

5. Wolfram is found in the following forms: WO_3, wolfram trioxide; Na_2WO_4, sodium wolframate; $CaWO_4$, calcium wolframate; and $(NH_4)_2WO_4$, ammonium wolframate.

When large doses of sodium wolframate (1.5-2.5 grams are introduced per os in dogs, disturbances develop in the gastrointestinal tract (vomiting, diarrhea). A similar picture appears when small quantities are introduced intravenously. Disturbances of the nervous system predominate when sodium wolframate is introduced subcutaneously, i.e., convulsions, paresis, and paralysis. Continuous exposure to sodium wolframate causes diarrhea. A study of the comparative toxicity

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of wolfram trioxide, ammonium wolframate, and sodium wolframate showed that the latter was the most toxic due to its greater solubility.

Metallic wolfram, when introduced per os, to all intents and purposes is not absorbed; wolfram salts are absorbed and form deposits in the intestines and bones and, to a lesser degree, in the skin and spleen.

There is little data on the action of metallic wolfram on man. A case of dermatitis caused by metallic wolfram powder and a case of acute toxic poisoning in smelting 70-80 percent tungsten steel have been described. The symptoms recorded were lethargy, fever, asthenia of the cardiovascular system, albuminuria, and a spreading pustular rash on the arms and legs.

According to our data, workers exposed to the action of wolfram powder often suffer from irritation of the upper respiratory passages.

6. Zirconium is found in the following forms: ZrO_2, zirconium dioxide; K_2ZrF_6, potassium salt of zirconhydrofluoric acid; $Zr(SO_4)_2$, zirconium sulfate; $Zr(NO_3)_2$, zirconium nitrate; $ZrO_2Cl_2 \cdot 8H_2O$, chlorozirconyl. In pharmacology, zirconium dioxide is used in powder form in the treatment of wounds and as a contrast medium in gastric roentgenography.

There is no literature on the action of zirconium and its compounds on animals. According to our preliminary data, subcutaneous injections of zirconium salts in rats cause necrosis at the site of injection. The local effect of zirconium sulfate is particularly active. Emaciation and a reduction in hemoglobin and red count are observed in cases of continuous use of zirconium salts (in doses of 100 milligrams of zirconium per kilogram of weight). The introduction of similar doses of chlorozirconyl caused pronounced emaciation after 15 to 18 days and death after 30 to 35 days. Continuous subcutaneous injection of metallic zirconium caused emaciation in rats.

There is no data on the action of zirconium and its compounds on man.

7. Cobalt is found in the following forms: $CoCl_2$, cobaltous chloride; $Co(NO_3)_2$, cobalt nitrate; $CoSO_4$, cobalt sulfate; and $CoCO_3$, cobalt carbonate.

Cobalt in small doses stimulates hemopoiesis. It is found, in very small quantities, in plant and animal tissues. It is a biologically important element for certain animal forms, and its absence leads to progressive emaciation. Cobalt is linked with the synthesis of insulin in sheep and large horned cattle. Cobalt is used in veterinary practice for the treatment of enzootic marasmus (coast disease, bush sickness). It is a hemopoietic agent. When metallic cobalt is introduced per os and subcutaneously in an animal, hemopoiesis is at first intensified (increase in hemoglobin and red count) and then inhibited. A single introduction of a large dose of cobaltous chloride (60 milligrams or more) is fatal to rabbits. Continuous mithridatic introduction of small doses of cobaltous chloride causes gradual intoxication and death after $2\frac{1}{2}$ to 3 weeks. Clinically, intoxication is manifested by myasthenia, lethargy and convulsions.

Cobalt acetate powder causes, in man, nausea, vomiting, abdominal cramps, and fever. Metallic cobalt powder causes dermatitis. Specific sensitivity to cobalt takes place. According to our data, acute and chronic action on the gastrointestinal tract, kidneys and upper respiratory passages is also possible.

8. Antimony is found in the following forms: Sb_2O_3, antimonious trioxide; $SbO(C_4H_4O_5K) \cdot \frac{1}{2}H_2O$, tartar emetic; Sb_2O_5, antimonic pentoxide; Sb_2S_3, antimonous sulfide; Sb_2S_5, antimonic sulfide; $SbCl_3$, antimonous chloride; and SbH_3, antimony hydride (stibene). In pharmacology it is used as an emetic and parasitotropic in kala-azar and other trypanosomiases.

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Relative lymphocytosis, eosinophilia and a slight increase in the red count are observed in cats subjected to metallic antimony. Continuous exposure to tartar emetic causes marasmus, growth inhibition and finally death in the case of rats. Continuous exposure to antimony trioxide and antimony pentoxide causes indigestion; trivalent antimony is more toxic than pentavalent antimony. Irritation of the mucous membranes, conjunctivitis, and corneal opacity are caused by metallic antimony vapors. Antimonious trioxide causes panting, vomiting, and hemic diarrhea in dogs. Organic antimony compounds have an irritating action.

Leucocytosis and thrombopenia are observed in man. Antimoniferous powder causes erythremia, pustules, and purulent sores on exposed parts of the body. Conjunctivitis and corneal opacity are caused by antimony vapors and antimonous chloride. The following secondary phenomena are observed in cases treated with tartar emetic: rheumatic pain, pertussis, urticaria, herpes, vasodilatation, and cardiasthenia.

9. Cadmium is found in the following forms: CdO, cadmium oxide; $CdSO_4$, cadmium sulfate; CdS, cadmium sulfide; and $CdCO_3$, cadmium carbonate. Cadmium is contained in the organs of normal men and animals, primarily in the liver (from 0.01 to 4.058 milligrams per 100 grams of ash). Cadmium enters into the composition of the dissociating, easily decomposing lipoprotein complex. Arginase activity depends upon the amount of cadmium present.

Large doses of cadmium salts, independent of the method of introduction into the organism, cause vomiting, diarrhea, atonia, and death in animals. Chronic cadmium posioning is manifested by gastroenteritis and marasmus. Dissection reveals fatty degeneration of the liver. Cadmium salts affect the central and vegetative nervous system. Cadmium is deposited in the liver and kidneys.

Irritation of the respiratory passages, cardiasthenia, cephalalgia, and hematuria are observed in acute poisoning by cadmium vapors. This poisoning sometimes results in death. Fatty degeneration of the liver and nephritis are observed upon dissection.

In cases of poisoning by cadmium carbonate pulver, the following symptoms appear: vertigo, opnea, vomiting, hemic diarrhea, general prostration, acrocyanosis, and convulsions. Some cases result in death.

Pain in the epigastric region, nausea, constipation, and anorexia (observations at zinc casting shops) are caused by continuous exposure to cadmium oxide.

There is no available data concerning the action of gallium, titanium, tantalum, niobium, and a number of other rare metals upon the living organism.

The data above is only an introduction to the systematic study of important new problems in the production and use of rare metals from the standpoint of labor hygiene. However, it may give practical workers in industrial sanitation inspection (doctors of medico-sanitation sections and health stations) some information as to correct organization of work to make working conditions healthful at enterprises.

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